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(54) Treating keratinous fibres

(57) Methods and compositions are disclosed for finishing textile articles on keratinous fibres by treating the articles with an isocyanate functional anti-felt prepolymer and an organophosphorus flame retardant agent and/or a flurocarbon water- or oil-repellent. The finish imparts wind resistance together with flame retardant and/or water and oil repellency.

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SPECIFICATION

Treating keratinous fibres

This invention relates to a method of treating keratinous fibres to render textile articles made of such fibres resistant to area felting shrinkage and also impart other desirable properties such as water-and-oil-repellency and/or flame retardancy.

Many methods for rendering wool textiles shrink-resistant are known. These generally fall into two broad categories: those involving degradative treatments with oxidising agents, e.g. chlorine, and those involving treatment with a polymeric compound or resin, e.g. the polydimethylsiloxanes of UK Patent Nos. 1396509, 1434017 and 1436694. Oil-and-water-repellency treatments have also been applied to wool textiles but these are generally incompatible with shrink-resist finishes since degradative finishes adverseley affect the water repellency, and resin treatments often affect the oil repellency. Similarly most resin treatments adversely affect flame-retardancy properties and are incompatible with flame-resist agents.

For uses, for instance industrial clothing, where laundering at relatively high temperatures (e.g. 60°C) is usual it would be advantageous to have a flame-retardant and shrink-resistant finish capable of withstanding such laundering.

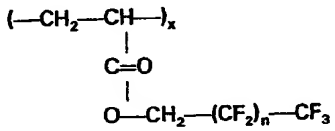
However, for textile articles destined for other end-uses, e.g. protective clothing where contamination from oil or oil/water emulsions is prevalent, it would be advantageous if all shrink-resistant and oil-and-water-repellent properties could be produced in the textile article. Further, if all these properties could be introduced at the same time, an extremely advantageous finish would be produced.

According to the present invention there is provided a method of finishing textile articles of keratinous fibres which comprises treating the articles with an isocyanate functional anti-felt prepolymer and an organophosphorous flame retardant agent.

The invention also provides a composition for treating keratinous textile articles comprising an organophosphorous flame retardant agent and an isocyanate functional anti-felt prepolymer.

Ideally the articles are also treated with a fluorocarbon agent. Fluorocarbon finishes confer water-repellent (hydrophobic) and oil-repellent (oleophobic) properties on textile fabrics, giving them the ability to repel both waterborne stains and those of an oily nature. The fluorochemicals have polymeric chains with a high percentage of replacement by fluorine atoms of the hydrogen atoms bound to the carbons. The oil repellency is due to the low surface energy found at the fluorine-rich surface of the fluorocarbon resin.

An example of an oil-and-water-repellent fluorocarbon is an acrylic polymer containing pendant fluoroalkyl groups, a feature which produces a low-energy, oil-repellent surface:



The length of the perfluoro chain is a factor influencing the degree of oil repellency obtainable. The longer the chain, the lower the energy at the fluorinated surface and the better the oil repellency. The chain should have at least four carbon atoms and should terminate in a $—CF_3$ group.

The water repellency property depends to a much less extent on the length of the perfluoro chain, and it is generally fairly constant for a particular series.

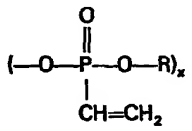
The agents are preferably applied simultaneously, but need not be. However, simultaneous application is advantageous in that separate processing steps are eliminated, giving a simple one-step "multi-finish".

According to another aspect of the invention there is provided a method of finishing textile articles of keratinous fibres which comprises treating the articles with an isocyanate functional anti-felt prepolymer and a fluorocarbon agent.

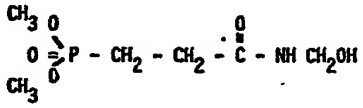
The invention further provides a composition for treating keratinous textile articles comprising a fluorocarbon agent and an isocyanate functional prepolymer.

The fluorocarbon agent may be one of the commercially available fluorocarbons used for imparting water-and-oil-repellent properties to textiles. We have found that such agents are incompatible with all current anti-felt or shrink-resist treatments for wool textiles, except those based on isocyanate functional prepolymers.

Any suitable organo phosphorous flame retardant agent may be employed but it is preferred to use one which may be cured to give a wash-fast finish. Examples include tetrakis hydroxy methyl phosphonium chloride and its analogues and, especially, oligomeric vinyl phosphates, such as:



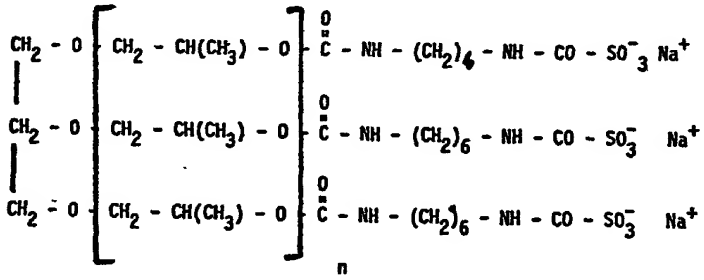
wherein x may be about 3 and 1 may be C_2H_4. Other organophosphorous agents which may be used include for example:



which, in itself, is not substantive to wool but may be cured using an auxiliary cross-linking agent.

Ideally the isocyanate functional prepolymer is a blocked isocyanate, and preferably is a water soluble blocked isocyanate. Especially preferred are the polycarbomyl sulphonates described in UK Patent No. 1419306. These may conveniently be prepared from polymeric di- or poly-isocyanates by treatment with sodium bisulphite.

Preferred polycaromoyl sulphonates have polyoxyalkylene, etg. polypropylene oxide, backbones and three carbomoyl sulphonate groups. Particularly preferred compounds have the following structure:



wherein n is about 13, available commercially under the same "Synthappret BAP".

The quantities of the various agents used may vary within wide limits depending on the substrate, end-use, co-reactants, etc., and will differ according to the agent. Thus the isocyanate functional anti-felt agent may be used in the range 0.1 to 10% o.w.w., especially 0.5 to 2% with 1% being preferred. The organo-phosphorous flame-retardant will generally require a fairly high add-on, in the range 10—30% o.w.w. with 15 to 20% being preferred. The fluorocarbon agent may be used in amounts up to 2% with 0.6 to 1.0% o.w.w. being preferred.

The above shrink-resist prepolymer is often applied together with a copolymer such as an acrylate or a soft polyurethane dispersion. However, if the multi-finish is to be flame-retardant as well as shrink-resistant and water and oil repellent, then the copolymer should be chosen to augment the flame-retardant agent. Suitable copolymers in this case are polyvinylidene chloride (PVDC) copolymers with acrylates containing at least 50% PVDC, which have a composition which is inherently more flame-retardant than the copolymers normally used.

The keratinous fibres may be for example mohair, alpaca, vicuna, angora or especially wool; and the textile article may be in the form of loose stock, slivers, slubbings, rovings, yarns, fabrics, made-up garment or carpets.

The treatment may be carried out in any suitable manner, e.g. dipping, spraying or padding, preferably the latter.

The invention will be illustrated further by the following Examples. The test methods used were as follows:

Felting Shrinkage

This was determined after 10, 25 and 50 cycles in a "Wascator" FOM 71" Washing Machine. Each cycle consisted of 30 minutes agitation at 60°C and normal wash rhythm, using 0.75 g/1 SM49 (a perborate free detergent) and three cold rinses (3 minutes each), liquor ratio 10:1, total load 3.9 kg with at least 1.95 kg of polyester makeweights. This test is considerably more severe than the usual test involving 1 hour or 3 hour washing in an International Cubex Washing Machine as this procedure is n t severe en ugh to simulate commercial laundering conditions.

Oil Repellency Test

The hydrocarbon resistance test AATCC 188—1975 with a scale from 0 (no oil repellency) to 8 (extrem ly high oil repell ncy) was used. A finish having an oil repellency rating of 4—5 is generally regarded as adequate for resistance to most common oily stains.

Water Repellent Test

The spray rating test was BS:3702 in which a scale of spray ratings 1 to 5 was used to described the water repellent effect. The higher ratings indicated better water repellency. The weight increase in percent during the test was also determined.

Wash Fastness

Samples were washed ten, twenty five and fifty times according to the procedure described above under "Felting Shrinkage".

Flame Resistance Test

This was evaluated according to Federal Aviation Regulations 25.853b, a vertical flame test with a 2 second ignition time. To meet this standard the after-burning time should not exceed 15 seconds and the char length should not be more than 8 inches, tested in both the warp and weft directions.

Treatments

Liquors were made with the amounts of agent shown in the Examples and applied to the wool fabric by padding to 80% pick-up, followed by drying and curing. The fabrics were then washed, in a Dyemaster washing machine using 10 g/l sodium perborate for 15 minutes at 30°C, at a liquor ratio of 1:30), and then dried.

EXAMPLE 1

A Wool gabardine fabric (260 g/m²) dyed with reactive dyes was padded with the following agents in the quantities listed in Tables I and II:

Synthappret BAP (Bayer)	(50% solids)
Impranil DLN (Bayer)	(soft polyurethane dispersion — 40% solids)
Nuva F (Hoechst)	(an anionic fluorocarbon, believed to be a Bunte salt ester of a fluorinated acrylate — 28% solids)
FC 214 AB (3M)	(a cationic emulsion of a fluorocarbon containing a water-repellent extender — 20% solids)

TABLE 1

Th Effect of Curing Conditions and Various Multi-Purpose Treatments on Shrink-Resistance, Water- and Oil-R pellency

Treatment	Curing Conditions	Area Felting shrinkage %			Oil Rating				Spray Rating		
		10W	25W	50W	B.W.	10W	25W	50W	B.W.	10W	25W
1% Synthappret BAP 1% Impranil DLN 0.3% Nuva F	110°C 10 min	0	3	32	5	6	1	0	3/9.4	3/12.4	
1% Synthappret BAP 1% Impranil DLN 0.3% Nuva F	120°C 10 min	0	0	7	7	6	5	4	3/10.7	3/14.2	3/20.9
1% Synthappret BAP 1% Impranil DLN 0.3% Nuva F	130°C 10 min	0	0	14	7	4	5	4	3/10.3	3/13.8	3/16.7
1% Synthappret BAP 1% Impranil DLN 0.3% Nuva F	140°C 10 min	0	0	10	7	5	5	4	3/9.8	3/14.8	3/17.8
1% Synthappret BAP 1% Impranil DLN 0.9% FC214AB	110°C 10 min	0	0	2	6	6	3–4	4	5/0.8	4/2.9	4/11.1
1% Synthappret BAP 1% Impranil DLN 0.9% FC214AB	120°C 10 min	0	0	1	6–7	6	4	4	£/1.1	4/3.6	4/12.6
1% Synthappret BAP 1% Impranil DLN 0.9% FC214AB	130°C 10 min	0	3	13	7	6	4	4	5/1.0	4/5.0	4/11.4
1% Synthappret BAP 1% Impranil DLN 0.9% FC214AB	140°C 10 min	0	0	3	7	6	4	4	5/1.9	4/3.7	4/13.4
1% Synthappret BAP 1% Impranil DLN	120°C 10 min	0	0	1	0	0	0	0	3/19.1	3/17.5	3/19.7
0.9% FC214AB	130°C 10 min	57	–	–	6	–	–	–	5/0.9	–	–
0.3% Nuva F	130°C 10 min	59	–	–	7	–	–	–	4/1.3	–	–
Untreat d	–	58	65	65	0	–	–	–	3/13.7	–	–

B.W. – before washing. 10W, 25W, 50W – aft r 10, 25 and 50 washes at 60°C.

TABLE II

The Effect f Fluorocarbon Concentration and Various Multi-Purpose Treatments on Shrink-Resistance, Water- and Oil-Repellency

Treatment	Curing Conditions	Area Felting shrinkage in %		Oil Rating			Spray Rating		
		10W	25W	B.W.	10W	25W	B.W.	10W	25W
1% Synthappret BAP 1% Impranil DLN 0.3% Nuva F	140°C, 5 min	6	12	7	6	3	3/13.3	-	-
1% Synthappret BAP 1% Impranil DLN 0.45% Nuva F	140°C, 5 min	6	13	7	6	5	3/11.3	-	-
1% Synthappret BAP 1% Impranil DLN 0.6% FC214AB	140°C, 5 min	7	13	4–5	4–5	4	4/2.3	-	-
1% Synthappret BAP 1% Impranil DLN 0.9% FC214AB	140°C, 5 min	7	12	6	6	5	5/0.6	-	-
3) 3% DCCA [1]	-	0	-	0	-	-	2/32.8	1/77.8	-
3) 3% DCCA, 0.6% Nuva F [1]	130°C, 5 min	0	-	6	6	2	2/12.5	2/23.8	-
3) 3% DCCA, 0.75% FC214AB [1]	140°C, 5 min	0	-	6	5	2	3/9.2	2/21.0	1/41.2
3) 3% Silicone, [2] 0.3% Nuva F	130°C, 5 min	2	-	0	-	-	-	-	-
3) 3% Silicone, [2] 0.75% FC214AB	140°C, 5 min	2	-	0	-	-	-	-	-
Untreated	-	58	66	0	-	-	3/13.7	-	-

1) Fluorocarbon applied by the exhaustion technique in acid conditions, DCCA treatment.

2) Silicone application – 3% Dicrylan 7013 (polydimethylsiloxane, Pfersee) and 3% A20& (aminosilane, Pfersee).

3) Felting shrinkage evaluated in Cubex, liquor ratio 1:15, pH 7, 3 hrs. Fastness to washing in a top loading washing machine at 40°C.

B.W. – before washing, 10W, 25W – after 10 and 25 washes at 60°C.

As can be seen from Tables I and II optimum results are obtained with a curing temperature between 110°C and 120°C for 10 minutes. The cationic fluorocarbon appears to be a more effective water repellent under these conditions. The control treatments, in Table I, show that the Sirolan BAP alone gives no water- or oil-repellent effect on wool; and the fluorocarbon alone cannot be washed because of excessive felting shrinkage.

An increase in the concentration of Nuva F slightly improved the fastness of the oil-repellent effect but the spray rating values were similar and not entirely satisfactory (Table II). The increase in the

concentration of FC214AB from 0.7 to 1% resulted in an improvement in oil and spray rating and the latter was superior to the treatment with Nuva F.

The chemical shrink-resist treatment (DCCA) adverseley affected the relatively good spray rating values for untreated wool. A treatment with Nuva F or FC214AB n DCCA treat d wool improved th wate-rep llent effect, although not as much as in the combination of Sirolan BAP and FC214AB. Also, the fastness of the water- and oil-repellent effect was less than with the multi-purpose finish based on Sirolan BAP and fluorocarbons. Similar results were observed on chlorine/Hercosett treated wool.

The combination of a silicone and fluorocarbon treatment gave an adequate shrink-resistance but the oil rating value was zero. This indicates that the polydimethylsiloxane polymer adversely affects the oil repellent effect of the fluorocarbons evaluated.

A multi-purpose finish based on the application of Sirolan BAP and fluorocarbons applied by a pad-dry-cure technique produced a very good shrink-resist, water- and oil-repellent effect, adequately fast to 50 very severe washings at 60°C. FC214AB gave a superior water-repellent effect to Nuva F.

EXAMPLE 2

An all-wool gaberdine fabric (275 g/m²) dyed orange with reactive dyes was padded with liquors containing agents as shown in Table III. All percentages are by weight on the weight of the fabric. Additional chemicals used were:

EDTA	disrodium salt of ethylene diamine tetra acetic acid
Fyrol 76 (Stauffer Chemicals)	an oligomeric vinylphosphonate
NMA	N-methylolacrylamide (60% solids)
Polidene 33- *** (Scott-Bader Co. Ltd.)	PVDC copolymers

TABLE III

Effect f Various Multi-Purpose Treatments on Flame-Retardance, Shrink-Resistance, Oil- and Water-Rep llency of Wool

Treatments	Flame-Retardance				Area Felting shrinkage in %	Oil-Rating		Spray-Rating			
	BW		50W					BW		25W	
	B.T.	C.L.	B.T.	C.L.	50W	B.W.	50W	W.I.	R	W.I.	R
0) Untreated	>15	F.L.	–	–	65	0	–	13.7	3	–	–
1) 20% Fyrol 76	1	7.5	–	–	45	0	–	83.7	1	–	–
2) 20% Fyrol 76, 6% NMA	0	6.3	–	–	36	0	–	75.6	1	–	–
3) 1% Synthappret BAP 1% Impranil DLN	>15	F.L.	>15	F.L.	1	0	–	19.1	3	19.7	3
4) 1% Synthappret BAP 1% Impranil DLN 1.0% FC214AB	>15	F.L.	>15	F.L.	1	6–7	3	1.1	5	12.6	4
5) 1.0% Synthappret BAP 2% Polidene 33–041 20% Fyrol 76	0	7.5	>15	F.L.	0	0	–	–	–	–	–
6) 1.0% Synthappret BAP 2% Polidene 33–041 20% Fyrol 76	1	7.5	0	8.8	1	0	–	66.8	1	64.8*	1*
7) 1.0% Synthappret BAP 2% Polidene 33–021 Fyrol 76 0.65% FC214AB	0	8.8	>15	F.L.	5	6	5	5.1	3	14.1*	3*
8) 1.0% Synthappret BAP 2% Polidene 33–004 15% Fyrol 76	0	6.3	0	8.8	5	0	–	68.5	1	70.1*	1*
9) 1.0% Synthappret BAP 2% Polidene 33–004 20% Fyrol 76	0	8.8	0	6.3	5	0	–	83.6	1	69.2*	1*
10) 1.0% Synthappret BAP 2% Polidene 33–004 15% Fyrol 76 0.65% FC214AB	3	10.0	4	11.5	0	6	6	6.2	3	20.1*	3*

TABLE III (Continued)

Effect of Various Multi-Purpose Treatments on Flame-Retardance, Shrink-Resistance, Oil- and Water-Repellency of Wool

Treatments	Flame Retardance				Area Felting shrinkage in %	Oil-Rating		Spray-Rating			
	BW		50W					BW		25W	
	B.T.	C.L.	B.T.	C.L.	50W	B.W.	50W	W.I.	R	W.I.	R
11) 1.0% Synthappret BAP 2% Polidene 33–004 15% Fyrol 76 0.65% FC214AB	5	7.5	0	8.8	1	6	6	8.9	3	19.3*	3*
12) 1.0% Synthappret BAP 2% Polidene 33–004 15% Fyrol 76 0.9% FC214AB	0	10.0	2	0	1	6	6	4.L	4	8.6*	3*
13) 1.0% Synthappret BAP 2% Polidene 33–004 20% Fyrol 76 0.9% FC214AB	1	7.5	2	7.5	1	5	5	2.3	4	6.7*	3*

B.T. — burning time in seconds

C.L. — char length in cm

F.L. — full length (25 cm)

B.W. — before washing

25W, 50W — after 25, 50 washes at 60°C

W.I. — weight increase in %

R — spray rating

* — after 10 washes at 60°C

The treatments 1 and 2 (Table III) imparted adequate flame-resistance to the fabric evaluated, but the natural water-repellency of wool was adversely affected. The treatment based on the application of Synthappret BAP and Impranil DLN offered excellent shrink-resistant properties, compatible with the oil- and water-repellent effect of FC214AB, but this polymer system (treatments 3 and 4) is not flame retardant.

The after-wash procedure with sodium perborate was desirable to improve handle, to achieve adequate shrink-resistance and fastness of the oil-repellent treatment and to improve the water-repellent effect in the presence of the fluorocarbon FC214AB. In the absence of Fyrol 76 adequate shrink-resistance, oil- and water-repellency was obtained without after-washing.

To improve the flame-retardant properties of this multi-purpose treatment, Impranil DLN, a polyurethane dispersion was substituted by various PVDC co-polymer emulsions (treatments 5—13) as auxiliary flame-retardants.

With the PVDC co-polymers containing at least 70% PVDC satisfactory flame-retardance was noticed, particularly with polidenes 33—004 and 33—021, without any adverse effect on shrink-resistance.

Incorporation of the fluorocarbon FC214AB to this multi-purpose finish, in the presence of the most suitable Polid ne PVDC co-polymers (treatments 7, 10—13), showed that, particularly in th pr sence of Polidene 33—004, containing 80% PVDC, it was possible to obtain fully washable, flame-

retardant and oil-r pellent wool with all the parameters being adequately fast to 50 severe launderings at 60°C. The addition of the fluorocarbon FC214AB also effectively counteracted, particularly at a 0.9% level, the adv rse effect of Fyrol 76 on the natural wat r repellency of wool.

Although this multi-purpose finish involves an add-on of around 20% the handle is only slightly affected and was judged by several observers as quite acceptable (treatment 8—13).

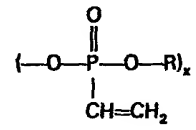
CLAIMS

1. A composition for treating keratinous textile articles comprising an organophosphorus flame-retardant agent and an isocyanate functional anti-felt polymer.

2. A composition as claimed in claim 1 in which the flame-retardant agent is curable to give a wash-fast finish.

3. A composition as claimed in claim 2 in which the agent is tatrakishydroxymethyl phosphonium chloride, an analogue of tetrakishydroxymethyl phosphonium chloride, or an oligomeric vinylphosphonate.

4. A composition as claimed in claim 3 in which the agent is



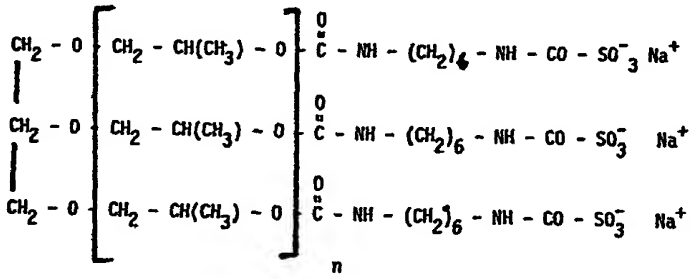
wherein X is about 3 and R is C_2H_4.

5. A composition as claimed in any one of claims 1 to 4 in which the isocyanate functional prepolymer is a blocked isocyanate.

6. A composition as claimed in claim 5 in which the blocked isocyanate is water soluble.

7. A composition as claimed in claim 6 in which the water soluble blocked isocyanate is a polycarbomoyl sulphonate.

8. A composition as claimed in claim 7 in which the polycarbomoyl sulphonate has the structure



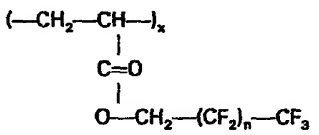
wherein N is about 13.

9. A composition as claimed in any one of claims 1 to 8 including a fluorocarbon agent.

10. A composition as claimed in claim 9 in which the fluorocarbon agent is an oil and water repellent fluorocarbon.

11. A composition as claimed in claim 10 in which the fluorocarbon is an acrylic polymer containing pendant fluroalkyl groups.

12. A composition as claimed in claim 11 in which the polymer has the formula



wherein the chain has at least four carbon atoms and terminates in a $—CF_3$ group.

13. A composition as claimed in any one of claims 1 to 12 in which a copolymer for the isocyanate functional anti-felt prepolymer is present.

14. A composition as claimed in claim 13 in which the copolymer used is a copolymer of polyvinaladine chloride with an acrylic containing at least 50% polyvinaladine chloride.

15. A method of finishing t xtil articles of keratinous fibres which comprises treating the articles with an isocyanate functional anti-felt prepolymer and an organophosph rus flame retardant agent.

16. A method as claimed in claim 15 which comprises treating the articles with a composition as claimed in any on of claims 1 to 14.

17. A method as claimed in either of claims 15 or 16 in which the isocyanate functional anti-felt prepolymer is used in the range of 0.1 to 10% oww, the organophosphorus flame retardant is used in the range of 10 to 30% oww and the fluorocarbonation, is used in the range of 0 to 2% oww.

18. A method as claimed in claim 15 in which the anti-felt prepolymer is used in the range 0.5 to 2% oww, the organophosphorus flame retardant is used in the range 15 to 20% oww, and the flurocarbonation is used in the range 0.6 to 1% oww.

19. A method as claimed in any one of claims 15 to 18 in which the keratinous fibres are mohair, alpaca, vicuna, angora, or wool.

20. A method as claimed in any one of claims 15 to 19 in which the textile article is in the form of loose stock, slivers, slubbings, rovings, yarns, fabrics, made-up garments or carpets.

21. A composition for treating keratinous textile articles comprising a fluorocarbon agent and an isocyanate functional prepolymer.

22. A composition as claimed in claim 21 in which the isocyanate prepolymer is that of claims 5 to 8.

23. A composition as claimed in either of claims 21 to 22 in which the flurocarbon agent is that claimed in any of claims 10 to 12.

24. A method of finishing textile articles of keratinous fibres which comprises treating the articles with an isocyanate functional anti-felt prepolymer and a fluorocarbon agent.

25. A method as claimed in claim 24 which comprises treating the articles with a composition as claimed in any of claims 21 to 23.

26. A composition according to claim 1 substantially as hereinbefore described with reference to and as illustrated in the foregoing examples.

27. A method according to claim 15 substantially as hereinbefore described with reference to and as illustrated in the foregoing examples.

28. A composition according to claim 21 substantially as hereinbefore described with reference to and as illustrated in the foregoing examples.

29. A method according to claim 24 substantially as hereinbefore described with reference to and as illustrated in the foregoing examples.

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